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The Adipic Acid Enhanced Limestone Flue Gas Desulfurization Process: An Assessment

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16. ABSTRACT

The paper gives an overview of EPA's testing of the adipic-acid-enhanced limestone flue gas desulfurization (FGD) process. Extensive research has determined that adipic acid, used as an additive to a limestone FGD system, improves system performance. Both SO2 removal and limestone utilization can be greatly increased by the buffering effect of adipic acid. Successful testing in laboratory-, bench-, pilot-, prototype-, and full-scale systems has demonstrated the benefits of this technology for new and retrofit applications. Although adipic acid degrades in the scrubber, no significant operating problems or environmental impacts have been identified. Economic estimates show the adipic-acid-enhanced limestone FGD system to be economically attractive, compared to conventional FGD systems. In addition, further research is underway to decrease the cost of using additives in FGD systems.

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Adipic Acid	Stationary Sources	07C
Flue Gases		21B
Desulfurization		07A, 07D
Calcium Carbonates		07B

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THE ADIPIC ACID ENHANCED LIMESTONE FLUE GAS DESULFURIZATION PROCESS

An Assessment

EPA-600/J-81-591
JOURNAL ARTICLE

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Extensive research has determined that adipic acid, when used as an additive to a limestone flue gas desulfurization (FGD) system, will improve the performance of the system. Both SO_2 removal and limestone utilization can be greatly increased by the buffering effect of adipic acid. Successful testing in laboratory, bench, pilot, prototype, and full scale systems has demonstrated the benefits of this technology for new and retrofit applications. Although adipic acid does degrade in the scrubber, no significant operating problems or environmental impacts have been identified. Economic estimates have shown the adipic acid enhanced limestone FGD system to be economically attractive when compared to conventional FGD systems. In addition, further research is underway to decrease the cost of using additives in FGD systems.

The majority of FGD systems that are either operating or under planning for utility use are calcium-based lime or limestone processes because of the system simplicity and economics.[1] Since lime is produced from limestone by an energy intensive calcination process, the direct use of limestone is becoming more attractive with the rising cost of energy. However, the performance of limestone scrubbers has been limited by reagent reactivity which results in low SO_2 removal efficiency, poor limestone utilization, and the ensuing reliability problems.

Extensive research has been conducted in the search for mass transfer enhancement additives that improve limestone scrubber performance. Adipic acid ($HOOC(CH_2)_4COOH$) was selected as the most attractive additive for research, development, and demonstration activities. Furthermore, it was found that the function of adipic acid is not adversely affected by forced oxidation and high chloride concentration. This gives the adipic acid enhanced limestone process advantages over other systems, such as the magnesium oxide promoted lime/limestone process, and makes it more suitable for closed-loop operation. Adipic acid has been tested in pilot-scale, prototype-scale, and full-scale limestone scrubbers and has demonstrated consistent improvement of system performance. The data indicate that the major benefits of adipic acid addition include:

- Increased SO_2 removal
- Decreased limestone consumption
- Decreased waste sludge volume
- Reduced operating cost
- Expanded FGD system flexibility

In addition, the adipic acid enhancement promotes the use of less expensive and less energy intensive limestone instead of lime. Further economic benefits can be obtained by the combustion of higher sulfur, less expensive coal without additional FGD equipment.

In order to promote this more advanced and more economical air pollution control technology and address properly the related environmental concerns, EPA's Industrial Environmental Research Laboratory-RTP (IERL-RTP) has conducted a comprehensive adipic acid program which has included the following six areas:

- Laboratory/theoretical investigation
- Scrubber testing and full-scale demonstration
- Degradation study
- Environmental impact and toxicity assessment
- Economic evaluation
- Alternative additives

The objectives of this paper are to report the highlights of EPA's adipic acid program and to discuss the recent development of the adipic acid enhanced limestone FGD process.

Laboratory/Theoretical Investigation

The major objectives of the laboratory/theoretical investigation were to understand the basic function of organic acid additives in limestone scrubbers and to search for the optimum additive.

Chemically speaking, limestone scrubber performance was limited by two pH extremes: (1) low pH near the gas/liquid

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interface which decreases the SO_2 solubility and absorption rate; (2) high pH near the liquid/solid interface which lowers the limestone solubility and dissolution rate. The basic chemical concepts show that this predicament can be relieved by the application of a buffer additive which can moderate the slurry pH and thus enhance the solubilities and mass transfer rates. TVA conducted the initial laboratory work and the data indicated some promise for an organic acid enhanced system.[2] Rochelle[3,4] performed a theoretical analysis and suggested the following criteria for the selection of organic acid additives:

- Proper solubility
- Low volatility
- Chemical stability
- No toxicity
- High availability
- Low cost

Table I. Comparison of the effectiveness and costs of 11 potential organic acid additives.[6]

Organic acid	Concentration required[a] (mM)	Price[b] ($/lb-mole)	Relative cost
Acetic	14.3	11.4	0.37
Formic	17.7	12.9	0.51
Sulfosuccinic	7.8	44.1[c]	0.77
Phthalic	6.4	58.1[d]	0.84
β-hydroxypropionic	14.5	28.8[e]	0.94
Adipic	7.0	63.5	1.00
Sulfopropionic	16.1	28.8[e]	1.04
Benzoic	15.8	36.7	1.30
Glycolic	22.4	30.4	1.53
Succinic	7.3	106.0[f]	1.74
Lactic	24.7	73.8	4.10

[a] Basis: SO_2 removal equivalent to 7 mM of adipic acid enhancement
[b] *Chemical Marketing Reporter*, July 2, 1979
[c] Maleic anhydride
[d] Phthalic anhydride
[e] Acrylic acid
[f] Succinic anhydride

Under the sponsorship of EPA, Chang and Rochelle[5] developed a mass transfer model and evaluated 11 potential organic acid additives.[6] Table I shows the relative effectiveness and costs predicted by the model. It is shown that acetic and formic acids are the least expensive potential additives but their expected high volatility may result in significant losses which would increase the probability of having significant economic and environmental impacts. Phthalic acid also appears to be attractive but is more likely to result in environmental problems because of its aromatic structure. Lactic, benzoic, glycolic, and succinic acids are economically unattractive because of their high costs. Sulfopropionic, β-hydroxypropionic, sulfosuccinic, and adipic acids were found to have suitable properties as buffer additives. However, the former three are not readily available in large quantities from the chemical marketplace. Therefore, adipic acid was selected as the most attractive organic acid additive.

The mass transfer model simulated the adipic acid function in limestone scrubbing by considering the following reactions:

$$\text{Sulfur dioxide + Water} \rightleftarrows \text{Acidity + Sulfites} \quad (1)$$
$$[SO_2 + H_2O \rightleftarrows H^+ + HSO_3^-)]$$

$$\text{Adipate ion + Acidity} \rightleftarrows \text{Adipic acid} \quad (2)$$
$$[^-OOC(CH_2)_4COO^- + 2H^+ \rightleftarrows HOOC(CH_2)_4COOH]$$

Reactions (1) and (2) show the buffering effect of adipic acid. As adipate ions react with the acidity (2) generated by the absorption of SO_2 (1), reaction (1) is shifted to the right and the SO_2 removal efficiency is enhanced. The mass transfer model predicted that less than 3000 ppm of adipic acid should be appropriate for significant SO_2 removal enhancement. The model also predicted that the SO_2 absorption rate would be higher under forced oxidation conditions due to less interference by the bisulfite ion. These two predictions were verified by data from actual scrubber testing.[7,8]

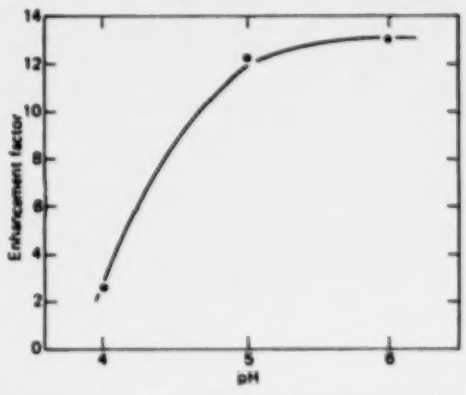

Figure 1. Limestone dissolution rate enhancement by adding 438 ppm of adipic acid.[9] (Enhancement factor = ratio of limestone dissolution rate with and without adipic acid.)

Chan and Rochelle[9] recently developed a theoretical model to describe the adipic acid function on limestone dissolution mechanism by the following two major reactions:

$$\text{Limestone + Water} \rightarrow \text{Alkalinity + Calcium ion + Carbonates} \quad (3)$$
$$[CaCO_3 + H_2O \rightarrow OH^- + Ca^{++} + HCO_3^-]$$

$$\text{Adipic acid + alkalinity} \rightleftarrows \text{Adipate ion + Water} \quad (4)$$
$$[HOOC(CH_2)_4COOH + 2OH^- \rightleftarrows {}^-OOC(CH_2)_4COO^- + 2H_2O]$$

Reactions (3) and (4) show that the adipate ions consumed by buffering the absorbed SO_2 as shown in Reactions (1) and (2) are replenished as alkalinity is generated by limestone dissolution. Due to those reactions, no adipic acid is consumed and the limestone dissolution rate is enhanced by the buffering effect. Laboratory experiments confirmed that the limestone dissolution rate was significantly increased by adipic acid in the absence of dissolved sulfites as shown in Figure 1. In the presence of dissolved sulfites, the relative effect of adipic acid will be less because the sulfites also enhance limestone dissolution.

Table II. Major operating ranges of adipic acid scrubber testing.

Adipic acid concentration, ppm	0–4200
Cl, ppm	0–17,000
Na, ppm	0–22,000
SO_2 (gas), ppm	1500–2900
Hold tank pH	4.6–6.2
L/G, L/m³ (gal/kcf)	2–12 (15–90)
Fly ash loading, g/m³ (gr/dscf)	0–13 (0–6)

Scrubber Testing and Full-Scale Demonstration

In order to examine the technical and economic feasibility of adipic acid enhanced FGD systems, IERL-RTP has conducted a series of scrubber tests consisting of bench (0.6 kW),

pilot (0.1 MW), prototype (10 MW), and commercial (20 and 200 MW) scales. It can be seen from Table II and Figure 2 that the adipic acid technology has been tested in a variety of scrubber sizes, types, operation modes, and operating conditions. The major results are summarized as follows:

- SO_2 removal efficiency—A significant increase of SO_2 removal was observed at every level of scrubber testing. The data show that small amounts of adipic acid are required to raise the SO_2 removal efficiency from 50 to over 95%. The recent full-scale demonstration showed that 90% SO_2 removal was attained in a Turbulent Contact Absorber (TCA) without packing spheres with the addition of 2500 ppm adipic acid (Figure 3).[10]
- Limestone utilization—A limestone utilization of more than 90% was achieved without sacrificing SO_2 removal efficiency. Adipic acid addition allowed operation of the limestone scrubbers at a lower pH range (4.8–5.5) which results in high limestone utilization, low scaling tendency and high reaction gain for automatic pH control.[11]

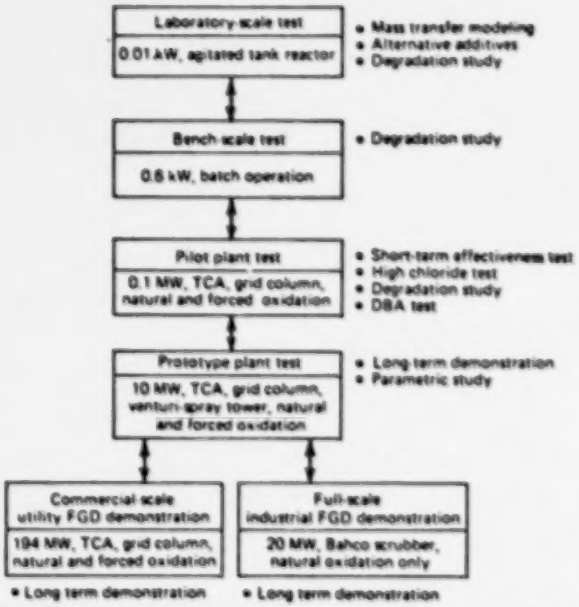
Laboratory-scale test
0.01 kW, agitated tank reactor
• Mass transfer modeling
• Alternative additives
• Degradation study
Bench-scale test
0.6 kW, batch operation
• Degradation study
Pilot plant test
0.1 MW, TCA, grid column, natural and forced oxidation
• Short-term effectiveness test
• High chloride test
• Degradation study
• DBA test
Prototype plant test
10 MW, TCA, grid column, venturi-spray tower, natural and forced oxidation
• Long term demonstration
• Parametric study
Commercial scale utility FGD demonstration
184 MW, TCA, grid column, natural and forced oxidation
Full-scale industrial FGD demonstration
20 MW, Bahco scrubber, natural oxidation only
• Long term demonstration
• Long term demonstration

Figure 2. Scenario of adipic acid scrubber testing and full-scale demonstration.

- High chloride testing—No significant difference in SO_2 removal was observed between runs at the IERL-RTP pilot plant with low (450 ppm) and high (13,000 ppm) concentrations of chloride.[12] The effectiveness of adipic acid in the presence of high chloride concentrations is an important factor since other additives, such as magnesium, are adversely affected by chlorides. The results of the tests confirm the suitability of adipic acid as an additive to closed-loop scrubber operation.
- Forced oxidation—The capability of forced oxidation to produce high quality waste sludge is another advantage of adipic acid enhancement over other additives such as sodium and magnesium. The pilot and prototype scrubber testing showed that the total adipic acid consumption rate is not significantly different between natural and forced oxidation conditions.[13,14]
- Long-term demonstration—Several long term (35 to 70 days), high performance adipic acid tests were carried out with both prototype and full-scale scrubbers. Continuous, smooth operation was sustained throughout each run without major operating problems. The data showed that adipic acid enhanced scrubbers can provide constant high performance under the normal load fluctuations experienced with the peaking operations of power plants.[10,15]

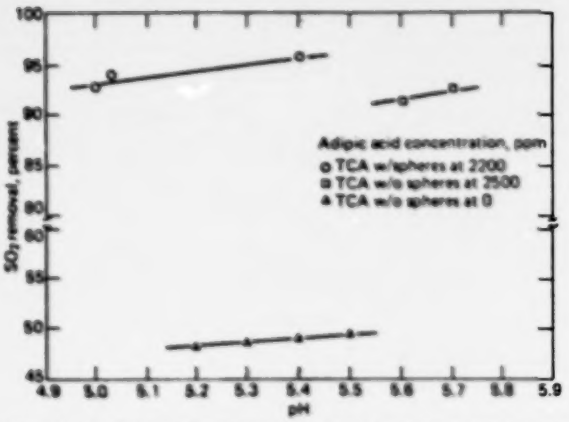

Figure 3. Scrubber performance of full scale TCA (200 MW) with and without packing spheres.[10]

Degradation Study

A material balance showed that an unaccounted-for adipic acid loss was occurring in scrubber testing.[16] Laboratory research has shown that the unaccounted-for losses were primarily caused by two mechanisms: (1) chemical degradation of adipic acid; and (2) occlusion of adipic acid and its degradation products in the precipitated calcium sulfite/sulfate solids. The first mechanism is responsible for most of the loss, especially under forced oxidation conditions.

The principal products of the degradation are glutaric acid ($HOOC(CH_2)_3COOH$), valeric acid ($CH_3(CH_2)_3COOH$), and carbon dioxide (CO_2). The valeric acid has a musty odor which is somewhat unpleasant; however, its concentration as a degradation product in the scrubber liquor is so low that the odor has not been a problem in testing to date. Other products that have been identified in trace amounts are succinic acid, propane, butane, methane, and carbon monoxide. Typical concentration of these products, measured at the prototype plant, is shown in Table III.[17] Theoretical analysis indicated that the degradation probably results from decarboxylation as the acid reacts with free radicals produced by oxidation of absorbed SO_2. This oxidative decarboxylation of adipic acid produces shorter molecules with fewer atoms in the chain.

Laboratory and bench-scale experiments showed that adipic acid degradation is affected by several important factors: degree of oxidation, temperature, adipic acid concentration, and inhibitors.[18,19] Forced oxidation accelerates the degradation rate but does not increase the adipic acid consumption to full-scale scrubbers because the degradation loss

Table III. Carbon compounds identified in scrubber when using adipic acid additive.[17]

	Adipic acid	Glutaric acid	Valeric acid	Succinic acid	CO[a]
Natural oxidation					
Liquid, mg/L	1,500	120	30	2	nd
Solid, μg/g	820	200	<3	<4	
Forced oxidation					
Liquid, mg/L	1,800	150	30	40	40
Solid, μg/g	40	<4	<3	<4	

[a] in oxidizer vent gas, ppm
nd—not detected

is more than compensated by tighter water balances and less occlusion losses. The degradation inhibition effect of manganous ion at a pH below 5.0 was first verified at the Univesity of Texas at Austin's laboratory and IERL-RTP's pilot plant.[16,18] The presence of manganous ion is known to alter the mechanism of free radical initiation and propagation during SO_2 oxidation and probably results in fewer radicals in the limestone slurry. Research at the University of Texas at Austin, under an EPA cooperative agreement, showed that 10 to 15 ppm of manganous ion present at pH 4.6 can reduce the adipic acid degradation rate by two thirds.[18] Data from bench-scale scrubber field studies confirmed the manganous ion effect under both natural and forced oxidation conditions.[19] Analysis of slurry samples from the prototype plant showed that manganese concentration, probably leached from the fly ash, accumulated up to 57 ppm.[14]

Environmental Impact and Toxicity Assessment

No significant incremental environmental impact is anticipated when adipic acid is used as an additive in limestone scrubbers. The low concentrations of adipic acid in limestone slurries minimize any possibility of secondary environmental impacts.

In order to determine if solid waste from adipic acid enhanced limestone scrubbers should be classified as a hazardous waste, sludge samples from the prototype plant were analyzed according to the Extraction Procedure Toxicity Test as prescribed by regulations pursuant to the Resource Conservation and Recovery Act (RCRA). The results of the analysis are listed in Table IV.[20] It is seen that most of the elements are not significantly different between extracts from sludges with and without adipic acid and that they are all considerably lower than the concentration deemed hazardous.

In order to evaluate further the impact of adipic acid addition, chemical and biological tests were conducted on samples from the prototype scrubber while operating with and without adipic acid addition. Samples were taken from the flue gas after the scrubber, the oxidation tank vent, the scrubber slurry, and the filter cake. The chemical tests included the standard Level 1 test series.[21] The only significant difference in the chemical analysis was that more polar organic material was emitted in the flue gas from the adipic acid enhanced system;[22] however, the level emitted does not constitute an environmental problem. The biological tests included: (1) the mutagenicity assay, (2) CHO clonal toxicity assay, (3) rabbit alveolar macrophage (RAM) cytotoxicity assay, (4) human cell cytotoxicity assay, (5) rodent toxicity, and (6) fresh water toxicity assay on algae, fish, and invertebrates. There was no significant difference in toxicity or mutagenicity between the samples containing adipic acid and its degradation products and samples from conventional limestone systems.[23] Confirmatory genetic toxicity assays were also conducted on the leachate from adipic acid enhanced and conventional limestone FGD systems. The tests included salmonella/microsome assay, saccharomyces can^r/his$^+$ dual assay, and salmonella uvrB repair assay. The results from these tests showed no genetic activity in the samples.[20]

It should be noted that adipic acid is included on the hazardous substances list which was promulgated by EPA pursuant to the Clean Water Act. This list was developed primarily to identify substances, which if discharged into lakes, rivers, and streams in sufficient quantities, would be toxic to aquatic organisms. The regulations require notification of EPA in the event of a discharge of the substance in greater than the designated reportable quantity. The reportable quantity for a discharge of adipic acid is 2270 kg (5000 lb). The fact that adipic acid is one of about 300 chemicals appearing on the hazardous substances list does not restrict its use in the nylon industry or even as a food additive. Likewise, it does not affect the use of adipic acid as an additive to FGD systems.

Worker exposure to adipic acid is not a problem. Dust inhalation can be controlled by a filter mask if necessary. The item most often associated with using adipic acid in FGD systems is the unpleasant odor which has been reported. The odor is probably a result of adipic acid's being degraded to valeric acid which has a very low threshold for odor detection. The odor has been reported occasionally at Shawnee prototype tests and Springfield utility FGD demonstration; however, it has not been a problem at either location. The odor was not noticed in the testing at Rickenbacker industrial FGD demonstration. The odor, or possibility thereof, should not constrain use of adipic acid in FGD systems.

Economic Evaluation

Based upon the data of prototype adipic acid testing, several economic comparisons of limestone FGD systems with and without adipic acid enhancement have been prepared.[8,24] These estimates show that for a new system with a 90–95% SO_2 removal requirement, both operating and capital costs for adipic acid enhanced systems are less than for conventional limestone systems. The lower costs for the adipic acid enhanced system are due to energy savings and to the reduced amount of limestone and solid waste. These projections do not incorporate any economic benefit to the increased operability and potentially decreased maintenance that would be expected with an adipic acid system. Further, economic benefits can potentially be accrued by burning higher sulfur, less expensive coal or from converting lime to limestone systems. In addition, systems with compliance problems may retrofit adipic acid addition relatively easily and bring a system into compliance with a minimal capital expenditure and in a brief period of time. Therefore, site specific factors may make the use of adipic acid very attractive.

Alternative Additives

In order to pursue more economic and chemically stable additives, IERL-RTP is conducting research on two promising buffers—dibasic acid (DBA) residue and glycolic acid.

DBA is the waste material or by-product of adipic acid or cyclohexanone manufacturing processes which contains an appreciable amount of organic acids. The market price of DBA is expected to be 40 to 50% cheaper than pure adipic acid. Four dibasic acids are currently being tested at IERL-RTP's pilot plant to evaluate and compare the effectiveness of DBA with pure adipic acid in terms of SO_2 removal efficiency and limestone utilization.[25] The preliminary results (Figure 4) show that DBA significantly enhances the SO_2 removal efficiency. If "meq/liter" is taken as the basis of organic acid

Table IV. Results of extraction procedure toxicity test.[20]

Extract	Concentration of element (μg/L)							
	Ag	As	Ba	Cd	Cr	Hg	Pb	Se
Sludge of limestone scrubber	1	47	<500	2	10	0.1	2	30
Sludge of adipic acid enhanced limestone scrubber	<1	54	<500	4	13	0.1	3	43
Hazardous waste criteria[a]	5,000	5,000	100,000	1,000	5,000	200	5,000	5,000

[a] *Federal Register* 45 (98) (May 19, 1980).

concentration, equivalent scrubber performance can be obtained between DBA and pure adipic acid promoted limestone systems. Further testing is scheduled to evaluate the degradation rate, toxicity, and economics of the DBA enhanced limestone systems.

Laboratory studies showed that glycolic acid ($HOCH_2COOH$) is not subject to chemical degradation under stimulated scrubber conditions. Pilot plant testing is under consideration to investigate the potential benefits of this nondegradable additive.

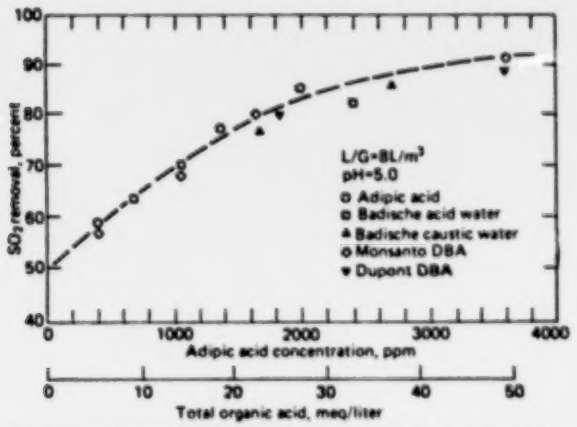

Figure 4. Effect of organic acid concentration on sulfur dioxide removal at the IERL-RTP pilot plant.[25]

Summary

The following conclusions are drawn from this review of the EPA adipic acid program:

1. Adipic acid is an effective mass transfer enhancement additive for wet limestone FGD systems. Both SO_2 removal and limestone utilization can be greatly increased by the buffering effect of less than 3000 ppm of adipic acid.
2. Adipic acid enhanced FGD systems have been extensively tested in a variety of limestone systems. Data show that most existing limestone FGD scrubbers should be able to benefit from adipic acid addition without major process changes. Data are also available to support the design of new systems based on the technology.
3. Adipic acid degradation is caused by oxidative decarboxylation. The degradation products did not pose any serious operating problems. Manganous ion leached from fly ash at a pH below 5.0 can reduce the adipic acid degradation rate.
4. No significant environmental impact from adipic acid enhanced FGD systems is expected. The test results show no significant difference in toxicity or mutagenicity in samples containing adipic acid and its degradation products and samples from conventional limestone scrubbing.
5. The addition of adipic acid should be economically attractive when compared to conventional FGD systems. Economic benefits can be derived from the savings on energy consumption, raw materials, solid waste reduction, and shifting to less expensive coal and limestone.
6. Research on other possible additives has identified waste dibasic acids and glycolic acid as potential additives for the enhancement of limestone FGD systems that provide benefits similar to adipic acid at a lower cost.

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